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Recent progress in the shaping and sintering of barium titanate nanoparticles. Application to high permittivity capacitors

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Abstract

The miniaturisation of electronic components required for many devices involves an increase their volumic efficiency. This work focus on the size reduction of capacitors. They are two ways for increasing the capacity of such passive components. One is to find materials with high permittivity, the other is to reduce the thickness of the films used in multilayers ceramics.

Barium titanate, BaTiO₃ (BT) nanoparticles were sintered using Spark Plasma Sintering (SPS) because the material presents interesting properties when obtained by SPS [1-3]. In this case, very unusual interesting dielectric properties, a so called “colossal” permittivity value up to several thousands. Moreover, no temperature dependence is observed. However, the values of dielectric losses are too high to consider industrial applications. In order to reduce these dielectric losses, different approaches have been proposed to control the chemistry of grain boundaries. We present here the structural, microstructural and electrical properties of ceramics sintered by SPS from BaTiO₃ powders elaborated by co-precipitation method. Different routes tested to improve the dielectric properties of the ceramics are presented and discussed.

On the other side, thick films of BT have been prepared. The objective of this work was to develop a BaTiO₃ material having an accurate particle size to reduce the thickness of sintered films down to

1 μm. The rheological properties of the slurry have been optimized and, thanks to a suitable tape casting process, homogeneous thin films of 1 μm thickness could be obtained. Some properties of the films are described.

Key words

BaTiO₃, dielectric properties, SPS sintering, thick films

Introduction

For electronic applications, there is still a challenge to search for high capacity materials, preferably made of ceramics, which show low losses and that are stable with temperature. There are two ways for increasing the capacity of those ceramics, the one is playing on the material itself and increasing the permittivity, the other is increasing the surface contact between the electrodes and the materials. We choose to play on both challenges. For that purpose, we start with a well known high dielectric material, barium titanate (BaTiO₃ or BT). The use of Spark Plasma Sintering (SPS) leads to BaTiO_{3-δ} oxygen deficient nanoceramics showing totally different properties from those of “conventional” sintered BT [4-6]. In fact, the material presents, at ambient temperature and at $f = 1$ kHz, unusual and interesting dielectric properties, with a so-called “colossal” permittivity value up to hundreds of thousands. Moreover, and contrary to what is classically expected and evidenced for this type of materials, no temperature dependence is observed. These properties were explained by the presence of space charges in such materials [7]. On the other side, thick films of BT were also prepared by tape casting. In that case, the challenge was to decrease the film thickness below 3 μm. The powder quality and the slip formulation were optimized. Rheometry is a powerful technique for estimating the influence of the species in the slurries and slips given. In fact, these systems are under the influence of attraction and repulsion forces that leads to forces that opposes to flow which is a prime condition for tape casting. Therefore, rheometric criteria are employed for determining dispersant concentration, solids loading, and predict the slurry and slip behavior under shear as it happens during the application of the slurries. The aim of this work was to prepare slurries with optimal slip formulation of BaTiO₃ in order to fabricate thinner thick films for multilayer ceramic capacitors

We present here the structural, microstructural and electrical properties of ceramics sintered by SPS (Spark Plasma Sintering) from BaTiO₃ powders

prepared by the co-precipitation method. We point out the major influence of the re-oxidation thermal treatment after sintering over the dielectric properties. We also show the achieved improvement obtained by tape casting. Finally the first results associated both tape casting shaping and Spark Plasma Sintering are presented.

Experimental section

The powders were prepared as follows. The starting materials, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Prolabo), TiCl_3 (Prolabo, $d=1.20$, % min= 15) were weighted in appropriate proportions. They were dissolved in water and the coprecipitation was performed by addition of a solution of oxalic acid dissolved in ethanol. The precipitated oxalate was separated from the liquid phase by centrifugation, then washed several times with ethanol and dried overnight at 100°C . The precipitated oxalate was transformed into oxide by calcination at 850°C for 4 h in air.

For comparison, BaTiO_3 powder was also supplied by Sakai Chemical Ltd, Japan. Two average particle size were used, 100 nm (BT01) and 200 nm (BT02). Three binary solvent systems were used: toluene/ethanol (TE), toluene/methanol (TM), and xylene/ethanol (XE). All these solvents were supplied by Fermont, Mexico. Five dispersant agents were tested.

Slip formulation is critical for rheological properties required in the tape casting process for obtaining films thinner than $3\ \mu\text{m}$ for fabrication for multilayer ceramic capacitors. The slip is prepared with the dielectric material, suspended in a mixture of solvent, dispersant, binder and plasticizer. The most important conditions of a tape casting slip involves a well dispersed homogeneous and stable system, low viscosity, shear thinning behavior and a high solids loading

In order to densify the BaTiO_3 nanopowders, spark plasma sintering (SPS) was carried out using a Dr. Sinter 2080 device from Sumitomo Coal Mining (SPS Syntx Inc., Japan). The main advantages of SPS in comparison with the conventional sintering method are the lower temperature and the shorter dwell time. Each nanopowder (0.9 g) was loaded in an 8 mm inner diameter graphite die. A sheet of graphitic paper was placed between the punch and the powder as well as between the die and the powder for easy removal of the pellet after sintering. The powders were sintered in vacuum (residual cell pressure < 10 Pa). A heating rate of $25^\circ\text{C}/\text{min}$ was used from 600 to 1150°C , where a 3-min dwell at the sintering temperature was applied. An optical pyrometer, focused on a little hole at the surface of the die, was used to measure and monitor the temperature. An uniaxial pressure of 50 MPa was applied. After 3 min dwell, the electric current was switched off and the pressure

was released. The as-sintered pellets presented a thin carbon layer due to graphite contamination from the graphite sheets. This layer was easily removed by polishing the surface. In a previous work, the presence of residual carbon due to SPS processing technique was determined through the spectrometric quantification of CO_2 and appeared to be very low with a concentration of 93 ppm. Samples appeared dark blue, due to the presence of Ti^{3+} caused by the reducing atmosphere used during SPS (low vacuum). To restore the oxygen stoichiometry, SPS pellets were annealed in oxidizing atmosphere.

The chemical composition of the different oxide powders (Ba/Ti ratios) was determined using induced coupled plasma spectroscopy (ICP-AES) with a JY 2000 HORIBA YVON JOBIN device. The particle size and the morphology of the powders were observed with a Field Electron Gun Scanning Electron Microscope (FESEM, JEOL JSM 6700F). The structure was determined by X-ray diffraction analysis using a Bruker D4 Endeavor X-ray diffractometer ($\text{CuK}\alpha=0.154056\ \text{nm}$ and $\text{CuK}\beta=0.154044\ \text{nm}$) from 20° to 80° (2-theta). The density of the pellets was determined by the Archimede method using a Kern ARJ 220-4M balance. Prior to electrical measurements, the ceramic disks were coated with thin gold electrodes (thickness $\sim 30\ \text{nm}$) by sputtering (Cressington 108 Auto). The relative permittivity and the dielectric losses were obtained from impedance measurement using an Agilent 42924A Impedance Analyzer in the range from 100 Hz to 40 MHz at room temperature and an applied voltage of 1V.

We used the sedimentation test, an adequate method, to screen formulation materials. Slurry fabrication along with materials selection is the critical step to achieve a good dispersion of ceramic particles since once that binder and plasticizer was added. The rheologic criteria developed in this work have proved to be reliable for slurry and slip design by the selection of low viscous, low elastic and stable formulations. This real slip formulation design for tape casting based on rehomeetric criteria are given: BT01 in toluene/ethanol with ABn graft copolymer at 4% and BL-5Z, BT01 in toluene/ethanol with phosphate ester dispersant at 2% and BI-5Z, BT01 in xylene/ethano with oligomeric ester at 2% and BL-5Z, BT02 toluene/ethanol KD-6 at 4% and BL-5Z, and BT02 toluene/ethanol PD 2206 at 2% and BL-5Z. The first step to achieve good quality ceramic is given by an adequate technique for formulation design.

Results

Powders

FEG SEM pictures of the calcined powder obtained from coprecipitation (Fig. 1) show that BaTiO_3 powder consists of small particles, of average grain size of 150 nm approximately. The particles are mostly agglomerated, due to partial sintering during the calcination procedure. X-ray diffraction patterns of the powders show that they crystallize in the cubic perovskite structure

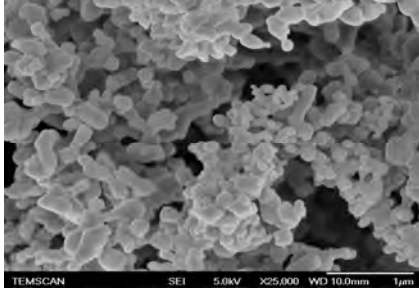


Fig 1. SEM FEG picture of the BT powder obtained by coprecipitation & calcination

Preparation of ceramics

The SPS technique offers the possibility to obtain ceramics with small grain size thanks to a lowest temperature and shortest time compared with the conventional sintering technique. As shown in our previous work, when elaborated by this technique, the ceramics exhibit unusual electrical properties with colossal relative permittivities of several hundred thousands at room temperature. The SPS takes place under vacuum atmosphere and the powder is introduced in a graphite die. As a consequence, the nanoceramics $\text{BaTiO}_{3-\delta}$ obtained are highly oxygen deficient which is easily evidenced by the dark blue color of the pellets. It is then necessary to perform a post-annealing treatment on these materials in order to re-oxidize the material. After this thermal treatment, such ceramics usually regain the original white color of the starting powder. No extensive studies have been focused this far on the optimization of the parameters of the post-annealing treatment after SPS. Most of the thermal treatment reported in the literature consists on heating the ceramics under an oxidizing atmosphere for a given time which is usually long, up to 12 hours.

The sintered materials obtained by spark plasma sintering (SPS) displayed a dark blue color due to the reducing sintering atmosphere. They present a high densification of 98%. The freshly fractured ceramics were observed by FEG-SEM (Fig. 2). The grain size is about 200 nm.

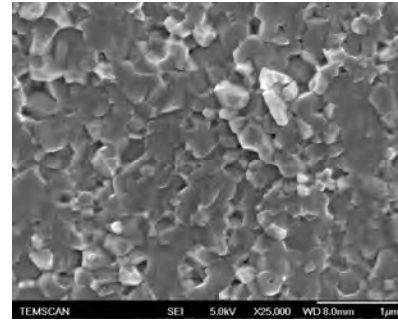


Fig 2. SEM FEG picture of the BT ceramic prepared by SPS

In the following, the electrical characteristics are given for a frequency of 1 kHz and at room temperature. After SPS, the as-sintered ceramics present colossal relative permittivities of $\sim 2.5 \times 10^6$. A first annealing process, taken from previous studies, is our reference. It is described as follow. The pellets are annealed at 850°C during 2 hours in air with a heating and a cooling rate of 150°C/h. Prior to annealing, the gold electrodes of the pellets have been removed in order to prevent an eventual diffusion of gold in the ceramics during the thermal treatment. After the annealing process, the ceramics remain dark blue. When processed in this particular way, the $\text{BaTiO}_{3-\delta}$ ceramics exhibit a relative permittivity of $\sim 3 \times 10^5$ and dielectric losses of 0.3. A complete study of the influence of different parameters of the annealing process (cooling rate, atmosphere, time) was performed [8].

Influence of the cooling rate

The influence of the cooling rate on the dielectric properties after the annealing process performed in air is shown in table 1. The ceramics were introduced in the hot furnace held at 850°C, during the dwell, and maintained at this temperature during only 5 minutes. Then, one ceramic was quenched in air while the other was cooled down with a low cooling rate (150°C/h). Higher relative permittivity is obtained for the quenched ceramic ($\epsilon_r = 3.2 \times 10^5$), up to three times the value of the ceramic cooled down slowly ($\epsilon_r = 1.1 \times 10^5$). However, the ceramics present very similar dielectric losses ($\tan\delta = 0.10$ for the quenched sample and $\tan\delta = 0.11$ for the one slowly cooled).

Cooling rate	ϵ_r	$\tan\delta$
slow ($\sim 150^\circ\text{C/h}$)	105 975	0.107
fast (quenching)	318 309	0.100

Table 1 : Dielectric properties of the ceramic annealed in air at 850°C during 5 minutes and slowly cooled ($\sim 150^\circ\text{C/h}$) or quenched

Influence of the atmosphere

The ceramics were annealed at 850°C for 5 minutes (one in air and the other in argon) and then cooled down slowly at 150°C/h. The dielectric properties of the ceramic annealed in air or argon are listed in table 2. The relative permittivities are similar with values slightly lower for the ceramic annealed in argon. Moreover, the values of the dielectric losses remain essentially the same, regarding the annealing atmosphere.

Annealing atmosphere	ϵ_r	$\tan\delta$
air	104 978	0.107
argon	88 370	0.191

Table 3 : Dielectric properties of the ceramic annealed in air and in argon at 850°C during 5 minutes and slowly cooled (~150°C/h)

Influence of the reoxidation time

The ceramic was annealed in air at 850°C for 5 minutes and then quenched. After the electrical measurements were performed, the sample (after removing the thin layer of gold) was introduced again in the furnace under the same conditions. The process was repeated several times until reaching a reoxidation time of 45 minutes. The relative permittivities and the losses of BaTiO_{3.8} ceramics at selected frequencies in air are listed in table 3 as a function of the annealing time at 850°C. The relative permittivity decreases when increasing the annealing time. It varies from $\epsilon_r = 3.4 \times 10^5$ for a reoxidation time of 5 minutes to 1.0×10^5 for a time of 45 minutes. On the contrary, the dielectric losses of the material are not influenced by the annealing time since the value of $\tan\delta$ remains close to 0.12.

Re-oxidation time (min)	ϵ_r	$\tan\delta$
5	340 724	0.100
10	324 066	0.122
15	279 322	0.121
30	145 971	0.118
45	103 408	0.115

Table 4 : Dielectric properties of the ceramic annealed for different time at 850°C in air followed by quenching

Giant permittivity was observed in various oxides, including perovskite [9]. In previous papers, we reported colossal permittivity values (1.10^5 at RT and 1kHz) for BaTiO_{3.8} ceramics (with composition Ba/Ti=1) sintered by SPS. The reduction state of the samples changes both their resistivity and relative permittivity. Bidault & al. [9] reported a value of $\epsilon_r = 1.10^5$ in reduced BaTiO₃ single crystals. The proposed mechanism to explain this unusual and high value is based on an interfacial polarization taking place at the grain boundaries involving polarons due to the presence of Ti³⁺.

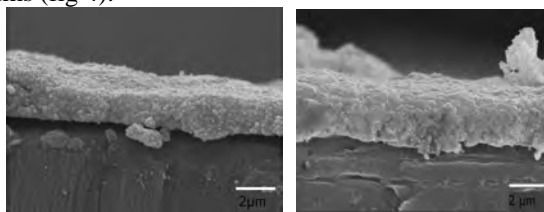
Those nanopowders were then sintered by SPS and the nanoceramics were obtained. It is well known that the use of a graphite die associated with low vacuum lead to a reducing atmosphere. The so obtained nanograin ceramics are even more likely to be reduced after the sintering process as evidenced by the dark blue color of the samples. The extremely high value of the relative permittivity determined at this stage has no sense since the ceramics do not behave like capacitors. The dielectric losses are too high to be measured. So the annealing treatment is necessary to lower these values, while trying to keep a value of relative permittivity as high as possible. This thermal treatment is crucial and should allow the partial reoxidation of the ceramics.

When the annealing treatment is performed, the oxygen vacancies formed during sintering diffuse towards grain boundaries (GB) that trap them. At some stage, the GB act as barriers against the oxygen vacancies diffusion and the overall mechanism of oxidation. The behavior of oxygen diffusion at the GB resulted from the GB acting as blocking barriers against oxygen diffusion. This blocking effect on oxygen diffusion at the GB seems to be related to the formation of complex defects between the acceptor-type defect and the oxygen vacancy. Regarding the reoxidation time, the most exciting part of this study is the demonstration that, after a reoxidation treatment of only 5 minutes, the electrical properties of the ceramics, whatever the composition, are completely modified. The relative permittivity is slightly decreased while the dielectric losses are completely modified, decreasing from values higher than 1 to 0.1. The most plausible mechanism to explain this behavior is the following. Since the materials contains a large amount of oxygen vacancies, a part of them coming from the powders and the additional part appearing during the sintering, a heating performed at 850°C even for a short period of time is enough to allow the motion of the oxygen vacancies towards the GB, that trap them and act as barrier diffusion. The localization of the oxygen vacancies in the GB explains the decrease of Ti⁴⁺ in the grain core, i.e. less Ti³⁺/Ti⁴⁺ couples, so a decrease of the relative permittivity and the

decrease of the losses, since the GB are now insulating. The cooling rate during the annealing process plays an important role on the final dielectric properties of the ceramics. Indeed, quenched samples showed higher relative permittivities than slow-cooled samples. The difference between the 2 batches of samples can be explained by the fact that the slowly cooled ceramics stay longer at higher temperature than the quenched ones. In fact, the electric behavior of the slowly cooled ceramics is close to the one of the samples that has been annealed for a longer time (i.e. 45 minutes, table 3) then quenched. So, it is not really the cooling rate that matters but the total duration that the ceramics spend at high temperature. The values of the main electrical characteristics, i.e. ϵ_r and $\tan\delta$, are also influenced by the atmosphere of the annealing atmosphere (table 2). The relative permittivity is not fundamentally different if air or argon is flushed during the treatment but the dielectric losses are lower in the case of air treatment. The motion of oxygen vacancies, related to oxygen diffusion, is probably lower in argon atmosphere, which is not surprising. Again, the reoxidation process is faster in air since the motion of oxygen vacancies, related to oxygen diffusion, is accelerated until they quickly end up, trapped at the GB.

Shaping of thick films

The optimized formulations were used for the preparation of thick films [10]. Different powders were used to determine the correlation between the film thickness and the roughness. The thickness were 2.1 μm and 2.5 μm for the powders BT 01 and BT02 respectively (fig 3). These low values could be obtained because the powder grain size was low. Some local thickness increase could be observed locally, and were attributed to the presence of aggregates in the powder. The use of filtration during the process, in order to retrieve the aggregates, allows reducing the roughness of the films (fig 4).



a) b)
Figure 3. FEG SEM pictures of a thick film made with a powder of a) 100 nm and b) 200 nm

In this section, we have demonstrated that the characteristics need for slip to be able to elaborate

films with a maximum thickness of 2 μm are : a low viscosity and a small elastic modulus. Moreover we show the use of a submicronic powder is not the only condition to obtain films with small thickness. The presence of aggregates is for example not wished.

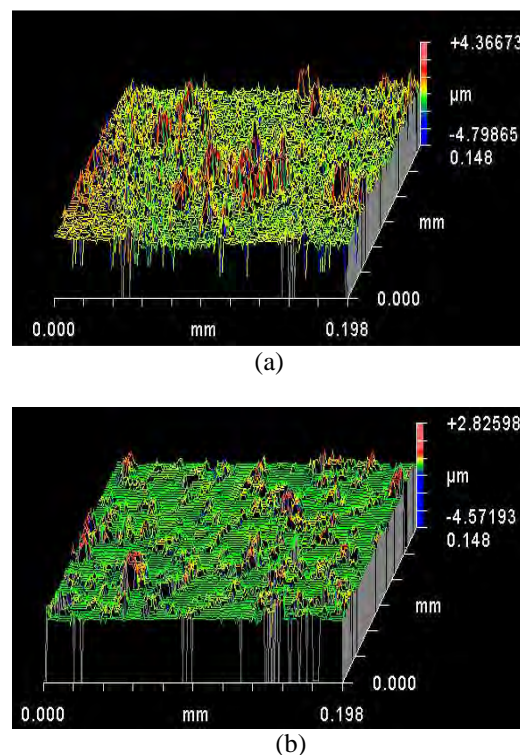


Figure 4. Images of the film's (made with a powder of a) 100 nm and b) 200 nm) surface. The aggregates appear red-colored

Combination of optimized shaping and spark plasma sintering

Recently, some experiments combining both SPS sintering and shaping by tape casting were performed. A multilayer structure was obtained by alternatively putting, in the graphite dye, silver powder and the barium titanate powder obtained by co-precipitation. The first results were encouraging. A common cycle could be used without altering the properties of the 2 powders. No cracks or microcracks were observed. A picture of the structure is shown in figure 5.



Figure 5. Multilayer structure obtained by SPS

Conclusion

Nanometric powders of barium titanate of controlled characteristics were obtained by a coprecipitation synthesis followed by a thermal treatment in air. The nanoceramics obtained by SPS present a densification of 98% and are highly oxygen deficient. The as-sintered ceramics do not show a capacitive behavior. It is necessary to perform an annealing treatment of reoxidation. The parameters (cooling-rate, atmosphere, time) of the annealing process of these ceramics were optimized. The number of oxygen vacancies associated with the amount of Ti^{3+} contained in the powders and ceramics and their localization at grain boundaries is the key factor to control the dielectric properties.

On the other side, we worked on the formulation design of barbotines for tape casting of ceramic layers thinner than 3 μm for multilayer capacitors. Particles of 100 nm and 200 nm of $BaTiO_3$ were mixed in different solutions of toluene, ethanol, methanol, xylene and water, with a dispersant and a PVB as bonding. Using oscillatory rheometry, an original experimental protocol was developed for formulating the slurries with appropriated rheological properties for thin tape casting. It was demonstrated that elastic contribution of viscosity must be small and that molecular weight of the bonding is the most important factor for reducing the viscosity of the non-aqueous slurries. The use of nanoparticles does not necessarily leads to the reduction of the layer thickness because of the formation of aggregates, which is not wished for the production of homogeneous bands. It was also demonstrated that the selection of solvent and dispersant is a function of the particle size of $BaTiO_3$. Films with a thickness as low 2 μm could be obtained by tape casting. The optimization of the overall process of elaboration of these dense nanoceramics has allowed obtaining very interesting properties for industrial applications.

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